

PATENT SPECIFICATION

NO DRAWINGS

1.170.858

1.170.858



Date of Application and filing Complete Specification: 5 June, 1967.

No. 25895/67.

Application made in United States of America (No. 557878) on 16 June, 1966.

Complete Specification Published: 19 Nov., 1969.

Index at acceptance: —A2 C(10X2, 20)

International Classification: —A 24 b 15/00

COMPLETE SPECIFICATION

Tobacco Substitute and Method of Making the Same

We, PHILIP MORRIS INCORPORATED, a Corporation organized and existing under the laws of the State of Virginia, United States of America, of 100 Park Avenue, New York, New York 10017, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a product for smoking in the form of a cigarette, cigar or cigarillo and also to a burnable sheet for use in such a product, as a tobacco substitute.

The nature of smoking products is such that the manufacture of a tobacco substitute is an extremely difficult operation. The subtleties of smoking and of producing a product which will be satisfactory to a smoker, *inter alia* from a taste and flavour aspect, make synthesis of such a product difficult. Thus, while many attempts have been made to prepare tobacco substitutes, none has resulted in the development of a satisfactory tobacco substitute.

The biological requirements for the growth of a tobacco plant are very different from the chemical and physical requirements for the generation of a smoke which is desirable to a smoker. Thus, there are often constituents in tobacco which result in a less desirable smoke from a smoker's viewpoint and which tend to affect adversely the character of smoke from tobacco products. Thus, tobacco, being a natural product, contains some constituents which would be better omitted, were the user of the tobacco given his choice. In addition, tobacco varies greatly from crop to crop, and even from leaf to leaf, in both its chemical constitution and its physical structure. It would clearly be most advantageous if a smoking product could be designed in such a manner that it has all of the desirable properties of tobacco, and none

of the undesirable properties. Such a synthetic product or tobacco substitute would make it possible to omit from the formulation those constituents which have an adverse affect, either biologically or organoleptically, and to permit the incorporation in the smoking product of those constituents which have been demonstrated to be desirable in smoke.

In accordance with the present invention, a tobacco substitute has been developed which can provide the satisfaction and smoking pleasure of natural tobacco and which, at the same time, can be free of undesirable properties often encountered in natural tobacco. Furthermore, the present invention provides a smoking product which is completely uniform and can be produced under controlled conditions.

According to the present invention, there is provided a product for smoking in the form of a cigarette, cigar or cigarillo which contains no tobacco plant parts and which comprises a mixture of from 5 to 95% by weight of a film-forming ingredient which is an acid gum having an acid value exceeding 30 mg. of potassium hydroxide per gram of gum, and from 5 to 90% by weight of a mineral ingredient, the balance, if any, consisting of compatible ingredients. The essential ingredients are thus (1) a film-forming ingredient and (2) a mineral ingredient. These two ingredients will be discussed in more detail below.

(1) The film-forming ingredient. The film-forming ingredient is preferably a pectinaceous material but may also be, for example, an alginic material. The film-forming ingredient must have an acid gum having an acid value in excess of 30 milligrams of KOH per gram of gum. One class of substances, the calcium-magnesium-potassium-sodium salts of the polyuronic acids, constitutes about one-third of the structural carbohydrate of leaf tobacco, and provides, in

[Price 4s. 6d.]

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reagent, which can be and preferably is, in aqueous solution, acts by forming a precipitate with the calcium or magnesium, in which case it can be a water-soluble monovalent metal salt of the formula M_nX wherein M is a monovalent inorganic cation, n is 1, 2 or 3, and X is an anion which may be monovalent or polyvalent, such that the calcium salt of the formula Ca_nX_n in which p and q are integers corresponding to the functionality of X is essential insoluble in the treating solution. Monovalent cations which are effective include the alkali metals such as sodium potassium and lithium, and ammonium and substituted ammonium ions $(NR_4)^+$, wherein R is aryl or alkyl. The anion portion of the molecule may be, for example, CO_3^{2-} , PO_4^{3-} , HPO_4^{2-} , or $H_2PO_4^-$. For example, the compound M_nX could be sodium carbonate, Na_2CO_3 , since sodium is a monovalent inorganic cation and calcium carbonate is essentially water-insoluble. Other examples include the orthophosphates, metaphosphates, and carbonates of sodium, potassium, lithium and ammonium. In the case of the orthophosphates, the anion portion of the molecule may be either PO_4^{3-} , HPO_4^{2-} or $H_2PO_4^-$. Specifically, for example, when ammonium orthophosphate is used, the precipitate is calcium and/or magnesium ammonium phosphate. The pH of this reaction mixture should generally be between 5.8 and 10 and the temperature should preferably be between 25°C. and 135°C., for a period of from 1 minute to 24 hours. Specific examples of precipitating agents which may be employed include sodium carbonate, potassium carbonate, lithium carbonate, ammonium orthophosphate, ammonium acid phosphate, and sodium orthophosphate.

In a second embodiment of this process, the reagent acts by sequestering the calcium or magnesium, thereby removing the calcium or magnesium atoms by forming a soluble complex therewith. Suitable reagents of this type include any sequestering agent which will form a complex or chelate with the calcium or magnesium thereby removing them and making them unavailable for re-cross-linking with the pectin. Such sequestering agents include ethylenediaminetetraacetic acid, alkali metal polymetaphosphates such as tetra-metaphosphates, hexametaphosphates and trimetaphosphates, pyrophosphates and tripolyphosphates, such as sodium hexametaphosphate, tetrasodium pyrophosphate and pentasodium tripolyphosphate. Many naturally occurring amines and peptides are also effective as sequestering agents for calcium and/or magnesium. Representative examples include alanine, aspartic acid, glycine, glycyglycine, glutamic acid, serine, tyrosine and di-iodo-L-tyrosine. Amino acids that are effective as chelating solubilizing

agents include betaalanine, N,N-diacetic acid; amino barbituric acid, N,N-diacetic acid; 2-amino-benzoic acid, N,N-diacetic acid; beta-aminoethyl-phosphonic acid; N,N-diacetic acid; beta-aminoethylsulfonic acid and N,N-diacetic acid. The pH of the reaction mixture should generally be between 4 and 10 and the temperature should preferably be between 0°C. and 145°C., for a period of from 1 minute to 24 hours.

A reagent may also function partially as a precipitating reagent, in accordance with the first embodiment and partially as a sequestering agent, in accordance with the second embodiment. Such a reagent, for example, is DAP (diammonium monohydrogen orthophosphate).

In a third embodiment of this process, the reagent is an acid which produces insoluble free pectic acid and soluble calcium and magnesium salts. Suitable such acids include inorganic acids, such as hydrochloric acid, phosphoric acid and sulphuric acid and similar acids which will form calcium and magnesium salts under the following conditions. The acid may generally be employed as 0.25 N to 5.0 N solutions, but is preferably employed as 0.5 N to 1.0 N solutions. The exact dilution and amount to be employed will vary with the particular acid which is used, it only being necessary that sufficient acid be present to convert the calcium and magnesium present in the tobacco being treated to the corresponding calcium and magnesium salts. The acid treatment is preferably conducted at a temperature of from -1°C. to 55°C. The acid treatment comprises reacting the tobacco parts with the acid until the resulting mixture has a pH of from 1.0 to 2.5. Preferably the pH is brought to from 1.0 to 1.7, the most desirable pH being between 1.15 and 1.55. This treatment will generally be conducted from 10 minutes to 24 hours, depending in part on the size of the tobacco particles.

Preferably, the resulting mixture is then washed with water. This water-wash step is preferably conducted at a temperature of from 15 to 35°C. and, preferably, distilled water is employed. When this wash step is employed, sufficient water should be used to remove the calcium and magnesium salts of the acids, thus, there should be at least 2 volumes of water per volume of the mixture resulting from the acid treatment. The wash water is separated from the tobacco by any suitable means, for example by conducting the wash in a centrifuge, filter press or Buchner funnel.

The mixture resulting from the acid treatment, and preferably after the water wash described above, is then suitably brought to a pH of from 2.7 to 10.5, by the addition of an alkaline material. Suitable alkaline

(2) The mineral ingredient. This ingredient, which is employed to provide the proper burning qualities and the proper ash to the smoking product, may comprise an alkali metal salt or an alkaline earth metal salt, for example, a calcium, sodium, potassium or magnesium salt, or a clay.

As can be seen from the preceding discussion of the film-forming ingredients, many of the materials employed as film-forming ingredients contain combined sodium, potassium, calcium or magnesium and thus may contain sufficient "mineral ingredient" for the purposes of this invention. This combined mineral, for example, a mixture of calcium pectate and potassium pectate, can be made into a tobacco substitute having satisfactory burning qualities. However, in most cases, the film-forming component will be supplemented with other minerals. In many cases it will be desirable and preferable to add water-insoluble minerals such as calcium and/or magnesium orthophosphates, pyrophosphates and polyphosphates. A particularly advantageous mineral ingredient is precipitated tricalcium phosphate (NF grade), which has been calcined at 1000°C. for three hours. These phosphates have the particular advantage of being able to release the small amounts of calcium and magnesium ions which may be necessary to extrude the compositions at the correct texture, which must be possessed by the formulation when it is cast on a steel belt or the like. This feature is especially important when the compositions do not contain fibre which ordinarily fulfills such a function. Examples of suitable alkali metal salts and alkaline earth metal salts, which, together with clays, are the preferred mineral ingredients, for use in accordance with the present invention include the following: potassium chloride, potassium sulphate, potassium phosphate, potassium nitrate, sodium chloride, sodium sulfate, sodium phosphate, potassium nitrate, calcium chloride, calcium sulphate, calcium phosphate, calcium nitrate, magnesium chloride, magnesium sulphate, magnesium phosphate, magnesium nitrate, lithium chloride, lithium sulfate and lithium nitrate. There are many clays which can also be used. Clays are mixtures of hydrated silicates of aluminium, calcium, magnesium and zinc usually with varying amounts of iron, manganese, cobalt or other heavy metals which often impart a heavy coloration. Common names of some useful clays are Kaolin, Montmorillonite, Bentonite, Attapulgite, Allophane and Illite. Usually it is desirable to use a light-coloured or white clay, and it may sometimes be found advantageous to use fired and reground clays because such treatment renders the polyvalent cations less available (i.e., soluble) and hence less likely to interfere with the performance

of the polyuronic acid constituent of the product.

A nicotine-donating ingredient is not essential but is a preferred ingredient. The nicotine may be added in any of the known ways of incorporating nicotine in tobacco. For example, it may be added *per se* to the tobacco substitute or it may be added in the form of a material which releases nicotine upon burning of the tobacco substitute. The latter method is illustrated in U.S. Patent 3,109,436, wherein the addition of a nicotine-exchange resin to tobacco is described. The nicotine may also be incorporated in other portions of the tobacco product, such as the filter or wrapper to accomplish the same result.

A non-essential but very preferred ingredient of the product is a plasticizer. The plasticizer is employed to provide the desired processing characteristics for the overall composition. Suitable plasticizers include certain tobacco extracts, obtained by leaching tobacco parts with water, or mixtures of solvents such as acetone, methanol or isopropanol with water, or by leaching tobacco parts in non-aqueous solvents, such as hexane, tetrachloroethylene and ethyl ether. Other plasticizing agents include monobasic, dibasic and tribasic acids, for example: lactic, malic, tartaric and citric acids. Additional plasticizers include glycerine, triethylene glycol, sorbitol, invert sugar, sucrose, oligosaccharides, triglyceride fats and oils, long chain fatty alcohols, linear paraffins, normal paraffins, paraffin waxes, beeswax, candlelilla wax, carnauba wax, sugar cane wax, maleates, citrates and corn syrup. Particularly desirable plasticizers are sodium citrate and potassium citrate. When one or more of these materials is employed, it has been found that the subjective evaluation of the taste and aroma of the smoke resulting from products incorporating the same has been favorable.

Other materials which may be included in the tobacco substitute include nicotine-containing extracts from tobacco leaf and other flavourants which add characteristics to make a desirable smoke. Such flavorants include, for example: licorice, deer tongue, flavouring oils or rum, chocolate and fruit essence.

The amounts of the essential ingredients in the products of the present invention are dictated by the types of materials used. For example, the polyuronic acid content is suitably from 20—70% of the total weight of the mixture. When a hygroscopic organic salt is used as the plasticizer, the preferred amount of polyuronic acid is about 50%. In general, the film-forming ingredient should comprise from 5 to 95% by weight of the composition.

The minerals in tobacco leaf which pro-

grams

454.0 triethylene glycol (TEG)

45.0 nicotine

- 5 57.0 bright tobacco extract (ethylene dichloride solubles) with hexane as the carrier.

The pH of the mixture was 4.7. The solids content was 6.35%.

- 10 The material was extruded onto an endless belt, partially dried with infrared heat, and then removed from the belt. Strips 8"—10" long were cut from the film and laid out to complete the drying process. The strips were then cut into cigarette filler.
- 15 The material processed well on a cigarette-making machine.

EXAMPLE 3

- 20 A series of formulations were prepared to determine the ratios of magnesium or calcium to potassium that would give the most effective burning characteristics to a film designed to substitute for tobacco filler in a cigarette. The binder made from each of the formulations was prepared by dispersing pectic acid and the calcium or magnesium hydroxides in hot tap water, then adding potassium hydroxide to a pH of 5.6. The mixture was heated on a steam bath, and an equilibrium pH of 6.5 was reached.

- 30 The material was cast by conventional casting procedures and either steam- or air-dried. The resulting film was shredded into cigarette filler, and made into cigarettes. The formulations and burning characteristics are given below:

- a. 51.5 g. pectic acid
7.1 g. potassium hydroxide
3.7 g. magnesium hydroxide.

- 40 The film that was formed held fire well, the "coal" and ash did not intumesce (puff up), and a compact white ash was formed.

- 45 b. When 4.7 g. of calcium hydroxide was substituted for the magnesium hydroxide in the formula above, the same burning characteristics were observed.

- c. 51.5 g. pectic acid
5.54 g. magnesium hydroxide
3.16 potassium hydroxide.

- 50 The film prepared from this formula did not hold fire well.

- d. 51.5 g. pectic acid
3.13 g. calcium hydroxide
9.52 g. potassium hydroxide.

- 55 The film from this formulation held fire well, the coal and ash intumesced (puffed up), and formed a dark ash.

- e. When 2.45 g. of magnesium hydroxide

was substituted for the calcium hydroxide in formula (d) above, the same burning characteristics were observed.

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EXAMPLE 4

Malic acid (268 g.) was dispersed in 20 litres of tap water in a Cowles Dissolver. The dispersion was neutralized with 272 g. of ammonium hydroxide solution. One-thousand grams of sodium polypectate (Product 6024, "Sunkist" [Registered Trade Mark] Growers) was added in the Cowles Dissolver and the mixture was agitated thoroughly. Twenty grams of nicotine, 50 g. of tobacco extract (ethylene dichloride extractables from bright tobacco leaf), and 208 g. of tricalcium phosphate were added in the order named. Colouring material was added to simulate the colour of cured tobacco leaf. The colours used were F, D and C dyes—No. 1 blue, No. 6 yellow, No. 2 red and No. 5 yellow. The resulting binder material had an equilibrium pH of 6.8. The binder was extruded on to an endless belt in a layer approximately 60 mils thick, dried with infrared heat, and then stripped from the belt with a doctor knife. The film, which was leathery and flexible with a wrinkled surface, was quite similar in feel and appearance to tobacco leaf.

The film was cut into 8"×12" sheets and allowed to equilibrate to 12% moisture. The sheets were then shredded into cigarette filler by making 25 cuts/inch. The filler was made into non-filter cigarettes on a "Haumi" [Registered Trade Mark] cigarette maker. The filler processed well as compared with regular cigarette filler from tobacco.

The cigarettes were tested for resistance-to-draw (RTD). RTD is defined as the pressure drop across a cigarette, expressed as inches of water when air flows through the cigarette at a velocity of 1050 ml/min. To determine this pressure difference one end of the cigarette was inserted into a specially designed tube through which air was drawn. The pressure difference between the open and enclosed ends of the cigarette was measured. A cigarette of the present invention was found, for comparison, to be about 25% lower than that of a commercial cigarette made from tobacco but was not so low that the cigarette did not perform sufficiently well.

The test cigarettes were weighed on an analytical balance in groups of forty cigarettes and the weights of the individual cigarettes were calculated and compared with the weight of the control. The test cigarette was slightly lower in weight than the control.

The test and control cigarettes were smoked on a constant volume smoking machine which takes a 35 ml. puff of two seconds duration once in 60 seconds. The smoke was trapped on a "Cambridge" [Registered Trade Mark]

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available cigarette used as a control were smoked on a constant volume smoking machine, the smoke was trapped, and the TPM determined as described in Example 1. The TPM from the test cigarette was about 50% of that from the control.

The puff count for the test cigarette and control was determined as described in Example 1. The count was slightly higher than that for the control.

The benzo (a) pyrene content of the smoke from the test cigarette was determined as described in Example 1 and compared with that from a control cigarette made from all-bright tobacco. The test cigarette had a benzo (a) pyrene content greatly reduced over that of the control.

The members of a smoking panel judged the cigarette subjectively and found the smoke mild and desirable.

EXAMPLE 6

Seven hundred grams of sodium polypectate was dispersed as described in Example 1. The ingredients listed below were added as described in Example 2.

350.0 g. sucrose
157.5 g. calcium pyrophosphate
210.0 g. triethylene glycol
14.0 g. nicotine
35.0 g. tobacco extract (ethylene dichloride solubles)
14 liters tap water

The equilibrium pH was 6.8.

This mixture was cast on an endless belt and partially dried with infrared heat. The film was removed from the belt with a doctor knife and dried further by air drying. The film was then cut into sheets and allowed to equilibrate to 12% moisture.

They were shredded into cigarette filler and used to prepare cigarettes.

The RTD of the cigarettes, determined as described in Example 1, was 0.9—1.0 inches of water. Their weight was about 75% that of standard cigarettes used as a control.

The TPM, determined as described in Example 1, was 31.1 mg/cigt. This was higher than the control which had a TPM of 21.8 mg/cigt.

The puff count, for the test cigarette, obtained as described in Example 1, was 11.3. The control had a puff count of 8.

The benzo (a) pyrene delivery of the test and control cigarettes (an all-bright tobacco cigarette), as determined chromatographically by the procedure given in Example 1, was 0.35 parts/million and 0.8 parts/million, respectively.

The test and control cigarettes were smoked by a test panel. The smoke from the test cigarette was judged mild and pleasing. It

had a slightly sweet taste and an aroma reminiscent of caramelized sugar.

While we do not wish to be bound by any particular theory, we believe that the sheet-forming material results in a desirable product because of the unique chemical and stereochemical properties of the natural pectic substances, algin and the like.

The pectins and algin are acids by virtue of the carboxyl groups attached at the 5th carbon position of their monomer units, whereas cellulose or hemicelluloses contain primary alcohol groupings, or methyl groups or hydrogen at this point. The carboxyl group is more readily attacked during low temperature pyrolysis than the corresponding groups of cellulose and hemicellulose; it also offers the possibility of combining ash producing cations and carbohydrate material into a single molecule.

The usual synthetic oxy-celluloses carry a partial complement of carboxyl groups at C₅, but retain some unchanged cellulose units, and other cellulose units in various states of oxidation and randomly esterified by nitrogen oxides. Thus, pectins are constitutionally different from competitive smoke-producing carbohydrate materials. They are also unique and different with respect to some specific stereochemical configurations which are known to produce large differences in response to pyrolysis. The pectins (in common with starch) possess an *alpha* structure at the C₁ carbon, while cellulose, hemicellulose, or oxycellulose have a *beta* structure at the C₁ carbon. That this difference is a very large one with respect to pyrolysis may be seen by comparing the different responses of starch and cellulose to pyrolysis. Starch forms low-temperature pyrolysis intermediates; i.e. thermal starch dextrins, with which a large area of starch technology is concerned; whereas cellulose decomposes at much higher temperatures without forming any similar materials.

The pectins are also different from starch or celluloses by reason of the different configurational arrangement at the C₄ carbon which gives the pectin polymer "*trans*" rather than the "*cis*" configurations which is found in starch. Thus, while the *alpha* configuration leads uniquely to a "*cis*" starch polymer, the same configuration leads to "*trans*" polymer structure in the case of pectins. Other relationships are evident from the following formulas which show the structural relationships of pertinent monomer units and polymers:



α D Glucose
(starch)

having an acid value exceeding 30 mg. of potassium hydroxide per gram of gum, and from 5 to 90% by weight of a mineral ingredient which is an alkali metal or alkaline earth metal salt or a clay, the balance, if any, consisting of compatible ingredients.

5 20. A sheet according to claim 19 having one or more of the features defined in any one of claims 2 to 8 and 10 to 16.

21. A burnable sheet according to Claim 10 19 substantially as hereinbefore described.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1969.

Published by the Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.